

Enhanced oxygen adsorption activity by CuO catalyst clusters on SnO₂ thin film based sensors

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Abstract

Resistance characteristics of thin film sensors based on uncoated SnO₂, SnO₂ with CuO overlayer and SnO₂ with CuO dotted clusters are compared in three different backgrounds of air, oxygen and vacuum. Measurements for the three sensor configurations are carried out as a function of temperature. The novel dispersal method of CuO catalyst in the form of dotted clusters is seen to enhance the oxygen adsorption activity on surface of SnO₂ thin film sensors. Conversion of molecular oxygen (O₂) to atomic oxygen (O) is shown to reduce the concentration of charge carriers in the conduction band of SnO₂ film. Co-existence of a greater amount of adsorbed oxygen on the SnO₂ film surface in conjunction with modulation of the space-charge region at the CuO-SnO₂ interface are attributed to influence the resistance of the sensor structures under reducing gas.

Keywords: Gas Sensor, thin films, adsorption, sputtering

1 Introduction

Thin films of semiconducting tin oxide (SnO₂) with suitable catalysts are known to exhibit high sensitivity to various reducing gases [1]. SnO₂ sensor is invariably anion deficient and the oxygen vacancies are mainly responsible for making available free electrons for the conduction process. Trace level detection of H₂S gas using semiconducting metal oxides including SnO₂ has gained a lot of importance [1] and its selective detection is known to be feasible after introducing suitable metal / metal oxide catalysts [2]. A review [2] on the available literature suggests the predominant use of CuO as the preferred catalyst material amongst others for sensing of H₂S gas using SnO₂. Some of the more extensively investigated sensor structures for H₂S gas detection include, mixed SnO₂-CuO powders [3], CuO-SnO₂ bi-layers [4], CuO-SnO₂ hetero-contacts [5] besides others. Action of CuO as a catalyst leads to enhanced H₂S sensitivity in SnO₂ thin films as a result of the co-existence of twin mechanisms; Fermi-level energy control and Spill-over [6]. Reducing H₂S gas reacts with CuO catalyst and converts it to CuS therefore varying the barrier height at the inter-granular boundaries after exchanging electrons (Fermi-level energy control mechanism) at the CuO-SnO₂ interface. Further, CuO catalyst surface dissociates the H₂S gas molecule and dissociated species (H⁺) then spills over on SnO₂ surface and reacts with the adsorbed oxygen thus influencing its conductivity (spill-over mechanism)[2].

However no efforts have been made towards understanding the influence of CuO catalyst on adsorbed oxygen on SnO₂ surface that may affect the

sensitivity and recovery of the semiconductor sensor. This study investigates the important role of the CuO catalyst towards enhancing the oxygen adsorption activity on surface of SnO₂ thin films resulting in improved response characteristics.

2 Experimental

SnO₂ thin films (90 nm) were deposited by reactive rf sputtering process under reactive gas mixture (Ar + O₂) on Platinum (Pt) interdigital electrodes (IDE) patterned on Corning glass substrates. Ultra-thin Cu metal was deposited onto the surface of SnO₂ thin films either as a continuous overlayer or in the form of dotted clusters and details are published elsewhere [2, 7]. It is important to note that conversion of Cu to CuO was achieved on SnO₂ film surface after a post-deposition annealing treatment in air at 300 °C for two hours. Three sensor configurations including SnO₂ film, SnO₂ with CuO overlayer and SnO₂ loaded with dotted clusters of CuO have been prepared and variation in sensor resistances investigated in three different backgrounds of oxygen, vacuum and air.

3 Results and Discussion

Figure 1 shows variation of sensor resistance in air for the three sensor structures in the temperature range 60 - 250 °C. It is interesting to note that both sensor structures having CuO catalyst (dotted and continuous) exhibit much higher resistance values in the entire temperature range in comparison to uncoated SnO₂ film sensor. This indicates that presence of CuO catalyst results in the reduction of charge carriers in the SnO₂ sensing layer in the vicinity of the IDEs and may be attributed to the formation of a depletion region at (p-type) CuO-SnO₂

(n-type) interface [2]. It is observed that SnO_2 - CuO (continuous) structure exhibits a higher sensor resistance in air in the temperature range 50 - 130 °C. However, a “cross-over point” is seen at 130 °C (figure 1) where the resistance of SnO_2 - CuO (dotted) sensor becomes more than those of other configurations. Contribution of depletion region towards increasing sensor resistance is expected to be a maximum for the structure having continuous p-type CuO layer on n-type SnO_2 film. However, the observed high resistance value of SnO_2 -CuO (dotted) sensor at higher temperature (> 130 °C) indicates that formation of depletion region alone is not responsible for obtained resistance values and that some other mechanism is also playing a dominant role.

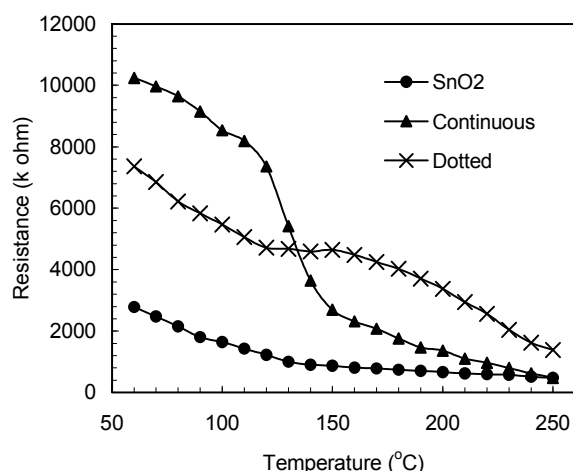


Figure 1: Resistance variation in air for uncoated SnO_2 , SnO_2 with CuO overlayer (continuous), and SnO_2 with CuO clusters (dotted) as a function of temperature

Resistance (R_p) of all the three sensor configurations has also been measured in different ambients i.e. in air (Rap), oxygen (Rop) and vacuum (Rvp) during both heating (60 – 250 °C) and cooling (250 – 60 °C) cycles. The variation of SnO_2 sensor resistance observed in different ambients is shown in figure 2 as a function of temperature. A relatively rapid decrease in resistance value (Rvp) is observed under vacuum during the heating cycle. The decrease in sensor resistance with temperature is attributed to semiconducting behavior of SnO_2 film. During cooling, resistance of SnO_2 film sensor follows the same trend (as observed in heating run) upto 130 °C (figure 2), whereas a significant deviation in the value of Rvp is observed below 130 °C. The lower Rvp value ($\sim 1.5 \text{ M}\Omega$) of SnO_2 film sensor at 60 °C during the cooling run in comparison to that observed while heating run ($\sim 3.0 \text{ M}\Omega$) i.e. a complete cycle is attributed to the substantial loss of adsorbed oxygen from the SnO_2 film surface under vacuum. Since the deviation in Rvp, during both heating and cooling runs, is observed at ~ 130 °C, hence it is reasonable to assume that enhanced oxygen activity on the SnO_2 film surface is triggered at ~ 130 °C. A decrease in

resistance with temperature (upto 130 °C) was observed for SnO_2 film sensor under both, air (Rap) or oxygen (Rop) ambient as well (figure 2). However, the same sensor (SnO_2 film) shows a remarkably distinct resistance variation during heating and cooling cycle under oxygen and air ambient over the temperature range 130 – 180 °C.

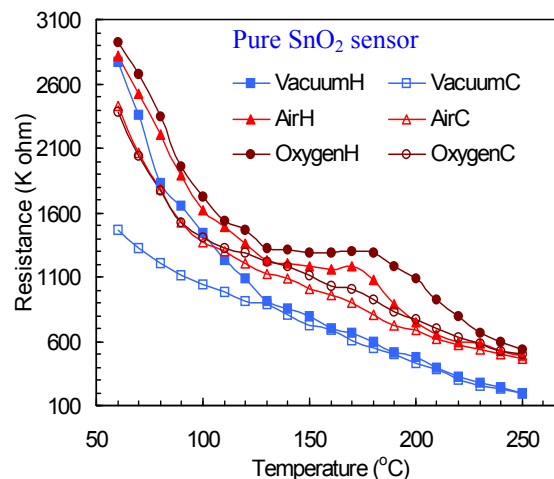


Figure 2: Resistance (R_p) variation of uncoated SnO_2 in different backgrounds of air (Rap), oxygen (Rop) and vacuum (Rvp)

A plateau region having constant value of sensor resistance (R_{op} and R_{ap}) with temperature is observed in figure 2 (in both air and oxygen ambient) which is contrary to the expected semiconducting behaviour. The presence of plateau region indicates, that the concentration of electrons in the conduction band of SnO_2 thin film is no longer increasing with an increase in temperature in the range 130 – 180 °C. The observed behaviour may be attributed to the competing effect due to presence of adsorbed oxygen on SnO_2 film surface which act as trap centres of charge carriers and becomes O_2^- after capturing an electron. One probable reason may be increase in the oxygen adsorption on the surface of SnO_2 sensor in the given temperature range due to presence of CuO catalyst.

However, the absence of plateau resistance region during the cooling run, rules out the possibility of extensive adsorption of oxygen on SnO_2 sensor surface in the range 130 - 180 °C. Therefore, the observed plateau region of sensor resistance may be due to the activation of conversion of adsorbed molecular oxygen (O_2) to atomic oxygen (2O^\cdot) at ~ 130 °C [8 - 10].

Figure 3 shows the variation of SnO_2 - CuO (continuous) sensor resistance as a function of temperature measured in different ambients (air, vacuum and oxygen). A continuous decrease in resistance was observed with increasing temperature in all ambients. No significant change in sensor resistance values is found during both heating and cooling runs even with different backgrounds. This

clearly indicates that presence of continuous CuO is protecting the underlying SnO₂ surface from atmospheric oxygen adsorption and sensor response remains same in different ambients (oxygen, air and vacuum) over the temperature 60 - 250 °C. The observed increase in resistance of SnO₂ - CuO (continuous) in comparison to uncoated SnO₂ film sensor can be attributed to the formation of a depletion region between p-type CuO layer and n-type SnO₂ film [2].

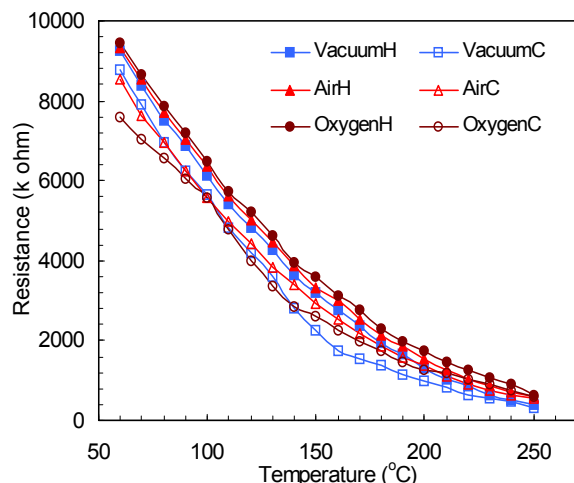


Figure 3: Resistance (R_c) variation of SnO₂ with CuO overlayer in different backgrounds of air (R_{ac}), oxygen (R_{oc}) and vacuum (R_{vc})

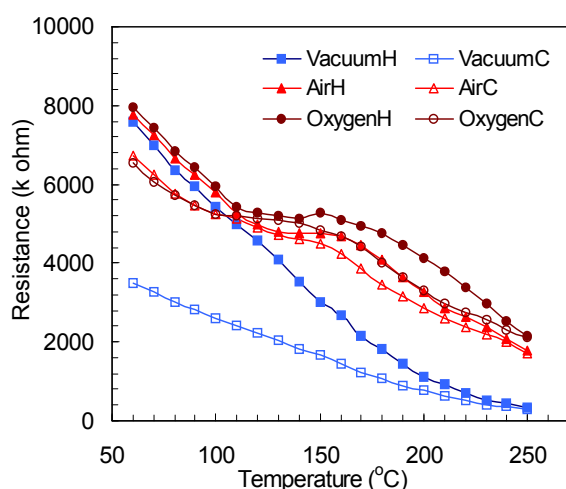


Figure 4: Resistance (R_d) variation of SnO₂ with CuO clusters in different backgrounds of air (R_{ad}), oxygen (R_{od}) and vacuum (R_{vd})

Variation in resistance values for SnO₂ - CuO (dotted) as a function of temperature under different backgrounds is shown in figure 4. It is noted that resistance characteristics are similar to those obtained for uncoated SnO₂ film sensor except with some critical differences. Specifically, the temperature where deviation between the resistance values (R_{vd}) observed under vacuum during consecutive heating and cooling runs (figure 4) is found to shift to higher

temperature (220 °C) in comparison to the value (130 °C) observed for uncoated SnO₂ film sensor (figure 2). The shift in deviation temperature shows the effective role of played by CuO catalyst in the form of dotted clusters towards increasing the concentration of adsorbed oxygen on SnO₂ film surface, thereby resulting in desorption of adsorbed oxygen at much higher temperature. It may also be noted from figure 4 that the plateau region having constant value of resistance observed under oxygen (R_{od}) and air (R_{ad}) ambient is shifted by about 20 °C towards the lower temperature range (110 - 160 °C) in comparison to uncoated SnO₂ film sensor. Furthermore during the cooling run a similar plateau characteristic (as observed during heating run) is noted in (figure 4); but with slightly lower magnitude. This is in contrast to the results obtained for uncoated SnO₂ film sensor (figure 2) where no plateau region of constant resistance was observed during cooling cycle (figure 2). The slightly higher value of plateau resistance obtained during heating cycle (in comparison to cooling cycle) is due to the additional contribution of the conversion of O₂⁻ to 2O⁻ besides the increase in concentration of adsorbed oxygen (charge carrier trap centres). These results confirm that the presence of CuO catalyst in the form of dotted clusters leads to enhanced adsorption of oxygen from atmosphere on the surface of uncovered SnO₂ in the temperature range 110 - 160 °C. The observed results on variation in sensor resistance with temperature clearly demonstrate the higher catalytic activity of CuO in the form of clusters towards adsorbed oxygen. It is also reasonable to believe that its presence is not only responsible for the formation of space charge layer at the CuO - SnO₂ interface but also enhanced concentration of adsorbed oxygen from the atmosphere (110 - 160 °C) on the surface of uncovered SnO₂ film.

4 Conclusion

CuO has been shown to possess high catalytic activity towards adsorbed oxygen. The novel dispersal of CuO catalyst in the form of dotted clusters on surface of SnO₂ films significantly increases the concentration of adsorbed oxygen in the temperature range 110 - 160 °C and exhibits plateau region in the resistance-temperature plot. The conversion molecular oxygen (O₂⁻) to atomic oxygen (O⁻) reduces the concentration of charge carriers in the conduction band of SnO₂ film and also results in irreversible plateau region. CuO in the form of dotted clusters is seen to catalyze enhanced adsorption of oxygen, thereby increasing negative charge density on stannic oxide surface and hence increasing the sensor resistance in air particularly at ~ 130 °C. Greater amount of adsorbed oxygen on the SnO₂ film surface besides modulation of the space-charge region at the CuO - SnO₂ interface allows realization of sensitive sensors for trace-level detection of reducing gas molecules at relatively low operating temperatures.

5 Acknowledgement

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6 References

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